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**(54) [Title of the Invention] Process for the Amination of Alcohols**

**(57) [Summary]**

**[Object]** An object is to provide a process capable of adequately suppressing the elimination and transfer reactions of alkyl groups at low temperature and low pressure and capable of aminating even low-boiling alcohols.

**[Constitution]** A process for the amination of alcohol, comprising reacting and aminating an alcohol with an amine in the gas phase, characterized in that the reaction is conducted in the presence of a solvent-impregnated catalyst at or below the boiling point of the solvent.

**[Claims]**

**[Claim 1]** A process the amination of alcohols, comprising reacting and aminating an alcohol with an amine in the gas phase, characterized in that the reaction is conducted in the presence of a solvent-impregnated catalyst at or below the boiling point of the solvent.

**[Claim 2]** The process as cited in Claim 1, wherein the catalyst is a hydrogenation catalyst.

**[Claim 3]** The process as cited in Claim 1 or 2, wherein the reaction is conducted in the presence of hydrogen.

**[Claim 4]** The process as cited in any of Claims 1 to 3, wherein the alcohol is a primary alcohol and/or secondary alcohol.

**[Claim 5]** The process as cited in any of Claims 1 to 4, wherein the amine is a primary amine and/or secondary amine.

**[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to a process for the amination of alcohol.

**[0002]**

**[Prior Art]** Processes that use an acid catalyst and processes that use a hydrogenation catalyst are currently known as alcohol amination processes.

**[0003]** Processes that use an acid catalyst generally require a high reaction temperature. In contrast, the reaction proceeds at a low temperature in processes that use a hydrogenation catalyst, but these processes also have various problems.

**[0004]** For example, a liquid-phase reaction requires a high pressure, which increases the cost of the reaction equipment. The alkyl groups are also eliminated and transferred during the reaction,

and an amine lacking in alkyl groups is known to be produced (Japanese Kokai Patent No. Sho 59-134754).

[0005] Even though the pressure is low in a gas-phase reaction, the alkyl groups are eliminated and transferred during the reaction in this case as well. It is important to control these reactions because an amine lacking in alkyl groups produced by elimination and transfer of the alkyl groups is difficult to separate and refine. A process of blowing hydrogen and amine into the reaction solution under normal pressure or slightly increased pressure and reacting while removing the water produced is a known process of controlling the elimination and transfer of alkyl groups (Japanese Kokai Patent No. Sho 56-152441). However, the reaction is carried out in the liquid phase, and it is essential that the water be removed. The reaction is consequently difficult to conduct when an alcohol with a boiling point lower than that of water, or an alcohol with a boiling point higher than, but close to, that of water is used as the raw material. The reaction also becomes difficult to conduct since it cannot be maintained in the liquid phase when an alcohol with a boiling point lower than the reaction temperature serves as the raw material.

[0006]

**[Problems That the Invention Is Intended to Solve]** It is difficult to say that the conventional processes attain a satisfactory level because the reaction temperature is high, the reaction pressure is also high, elimination and transfer reactions of the alkyl groups cannot be adequately suppressed, and the raw material alcohols are limited. These are not industrially satisfactory processes.

[0007] The object of the present invention is to resolve these drawbacks and provide a process capable of adequately suppressing the elimination and transfer reactions of alkyl groups at low temperature and low pressure and capable of aminating even alcohols with a low boiling point.

[0008]

**[Means Used to Solve the Above-Mentioned Problems]** As a result of in-depth studies of the amination of alcohols, the present inventors made the novel discovery that the elimination and transfer reactions of alkyl groups can be adequately suppressed at a low temperature, and an alcohol with a low boiling point can be aminated, by using a catalyst impregnated with a high-boiling liquid. The present invention was perfected on this basis.

[0009] Specifically, the present invention is a process for the amination of an alcohol comprising reacting and aminating an alcohol with an amine in the gas phase, wherein the reaction is conducted in the presence of a solvent-impregnated catalyst at or below the boiling point of the solvent.

[0010] The present invention will be explained in greater detail below.

[0011] The catalyst used in the process of the present invention is impregnated with a liquid that has a boiling point equal to or higher than the reaction temperature. The catalyst used is preferably a hydrogenation catalyst with a low reaction temperature. The term "hydrogenation catalyst" in the process of the present invention means a catalyst that has the ability to hydrogenate and dehydrogenate. The hydrogenation catalyst is not particularly restricted. Examples include those that contain elements such as Ni, Co, Cu, Fe, Cr, Zn, Pd, Pt, Ag, Ru, Rh, Ir, Re, and rare earth elements. Catalysts among them that contain Ni, Co, Cu, and Pd are especially preferred in terms of their activity and selectivity. These elements can be used individually or in combinations such as Ni-Co, Ni-Cu, Co-Cu, Ni-Re, Cu-Cr, Ni-Ir, and Ni-Pd. Other types of elements can also be added. There are various types of catalysts such as Raney catalysts, supported catalysts, flaked catalysts, sulfides, and oxides. [Catalyst] selection can be made in accordance with the types of raw materials and reaction.

[0012] The liquid that impregnates the catalyst should be one that has a boiling point equal to or greater than the reaction temperature, and that is liquid at the reaction temperature. Aromatic-based, aliphatic-based, polyether-based, polyamine-based, polyalcohol-based, silicone-based [liquids], and the like can be selected in accordance with the raw material alcohol used and the type of amine produced. The amount of liquid used is preferably a quantity that covers the pores and surface of the catalyst. The reaction rate drops when the amount of liquid is too large. The effect of the liquid diminishes and an amine lacking alkyl groups is produced when the amount of liquid is too small.

[0013] Contrary to ordinary solution reactions, this liquid must impregnate the catalyst prior to the reaction. However, it may also be supplied mixed with the raw materials when the liquid that has impregnated the catalyst is completely eliminated during the reaction.

[0014] A powdered or molded catalyst may be used in the present invention. Diatomaceous earth, alumina, silica, titania, zirconia, silica-alumina, and clay can be added for molding or to improve the filterability and durability of the catalyst.

[0015] The raw material is supplied to the catalyst by means a gas in the process of the present invention.

[0016] The raw material alcohol used in the process of the present invention is a primary or secondary alcohol. Tertiary alcohols slow the reaction rate and are not suitable for use. The number of carbon atoms is not particularly restricted and [the alcohol] may be either linear or branched. It may also contain aromatic rings. Examples include monofunctional alcohols such as methanol, ethanol, propanol, butanol, amyl alcohol, octyl alcohol, lauryl alcohol, myristyl alcohol, stearyl alcohol, behenyl alcohol, and oleyl alcohol; polyfunctional alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butanediol, hexanediol, glycerin, monoethanolamine, diethanolamine, and triethanolamine; and alcohols that contain aromatic rings such as benzyl alcohol and phenethyl alcohol. The aldehydes or ketones corresponding to the aforementioned alcohols can also be used in place of the alcohols because amination is conducted after oxidation to an aldehyde or ketone during the reaction in which these alcohols are aminated.

[0017] The amine used in the process of the present invention is preferably an aliphatic amine. Primary and secondary amines among them are especially preferred. Examples include methylamine, dimethylamine, ethylamine, diethylamine, propylamine, dipropylamine, butylamine, dibutylamine, dodecylamine, didodecylamine, ethyleneamine, and ethanolamine. The quantity of these aminating agents in relation to the alcohol is not restricted. It also poses no problem at all if these alcohols and amines are supplied as aqueous solutions.

[0018] Hydrogen must be added to the reaction system when a hydrogenation catalyst is used in the process of the present invention. Although the reaction progresses even when hydrogen is not added, the selectivity declines.

[0019] The water also need not be removed from the reaction system, but there is no problem if it is removed.

[0020] The reaction of the process of the present invention can be carried out either by a batch process or continuous process. A continuous reaction is preferred for its high productivity. It can be carried out in a fluidized bed, fixed bed, or moving bed.

[0021] It is difficult to define the reaction temperature in the process of the present invention because it varies greatly depending on the type of catalyst, raw material alcohol and ammonia, and amine. Nonetheless, 120-350°C is preferred, and 150-250°C is particularly preferred, in the

case of a hydrogenation catalyst. The selectivity declines due to amine decomposition when the temperature exceeds 350°C. A satisfactory reaction rate cannot be obtained when the temperature is less than 120°C.

[0022] The reaction pressure in the process of the present invention is preferably a pressure capable of keeping the raw materials in the gas phase. Too high a pressure is not desirable because the raw materials liquefy. The pressure therefore must be decided by taking into consideration the vapor pressure of the raw materials. An inert gas can also be added to gasify the raw materials.

[0023] After the resulting amine has been separated, the unreacted alcohol, reaction intermediates, excess amine, and hydrogen can again be supplied to the reactor in the process of the present invention.

[0024]

[Working Examples] The present invention is explained below by working examples. However, the present invention is not limited to these.

[0025] The following abbreviations are used for simplicity of expression.

[0026]

BDMAEE: bis(dimethylaminoethyl)ether  $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{O}$

DEG: diethylene glycol  $(\text{HOCH}_2\text{CH}_2)_2\text{O}$

DMA: dimethylamine  $\text{Me}_2\text{NH}$

DMAE: dimethylaminoethanol  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$

DMAEE: dimethylaminoethoxyethanol  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$

EG: ethylene glycol  $\text{HOCH}_2\text{CH}_2\text{OH}$

MAEE: methylaminoethoxyethanol  $\text{MeNHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$

TMEDA: tetramethylethylenediamine  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$

PEG: polyethylene glycol  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  ( $n \geq 3$ )

### Working Example 1

A catalyst in which 20% by weight of Cu as metal and 5% by weight of alumina were supported on a silica carrier was immersed for 24 hours at 60°C in PEG (average molecular weight: 1000). After thoroughly removing the excess PEG, 50 g of this catalyst was packed into

a Pyrex tubular reactor and heated to 190°C in a hydrogen stream (50 mL/min) under atmospheric pressure. 3 g/hr of DEG and 150 mL/min of DMA (anhydrous) were supplied thereto. The gas space velocity at this time was 130 hr<sup>-1</sup>. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 90%, and the selectivity was 76.6% for DMAEE and 15.5% for BDMAEE.

#### **[0027] Working Example 2**

A catalyst in which 15% by weight, 10% by weight, and 4% by weight of Ni, Co, and Cu, respectively, in terms of their metal content and 5% by weight of alumina were supported on a silica carrier was immersed for 24 hours in DEG. The catalyst was packed into a Pyrex tubular reactor and heated to 190°C in a hydrogen stream under atmospheric pressure. A mixed solution comprising 1 part (by weight) of DEG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 4500 hr<sup>-1</sup>. Hydrogen was supplied in a quantity that was 12.7 times the amount of DEG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 39%, and the selectivity was such that 3.2% of MAEE with eliminated methyl groups eliminated was produced.

#### **[0028] Comparative Example 1**

A catalyst in which 15% by weight, 10% by weight, and 4% by weight of Ni, Co, and Cu, respectively, in terms of their metal content and 5% by weight of alumina were supported on a silica carrier was packed into a Pyrex tubular reactor without immersion in DEG and heated to 190°C in a hydrogen stream under atmospheric pressure. A mixed solution of 1 part (by weight) of DEG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 6700 hr<sup>-1</sup> to bring the DEG conversion rate to substantially the same level as in working example 2. Hydrogen was supplied in a quantity that was 12.7 times the amount of DEG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 37%, and the selectivity was such that 7.7% of MAEE with eliminated methyl groups was produced.

### **[0029] Working Example 3**

A catalyst in which 20% by weight of Cu in terms of its metal content and 5% by weight of alumina were supported on a silica carrier was immersed for 24 hours in DEG. The catalyst was packed into a Pyrex tubular reactor and heated to 190°C in a hydrogen stream under atmospheric pressure. A mixed solution comprising 1 part (by weight) of DEG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 4500 hr<sup>-1</sup>. Hydrogen was supplied in a quantity 12.7 times the amount of DEG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 13%, and the selectivity was 95.3% for DMAEE and 3.5% for BDMAEE. No MAEE with eliminated methyl groups was produced.

### **[0030] Comparative Example 2**

A catalyst in which 20% by weight of Cu in terms of its metal content and 5% by weight of alumina were supported on a silica carrier was packed into a Pyrex tubular reactor without being immersed in DEG, and heated to 190°C in a hydrogen stream under atmospheric pressure. A mixed solution comprising 1 part (by weight) of DEG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 7100 hr<sup>-1</sup> to bring the DEG conversion rate to substantially the same level as in working example 3. Hydrogen was supplied in a quantity that was 12.7 times the amount of DEG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 14%, the selectivity was 95.3% for DMAEE and 3.2% for BDMAEE, and 0.6% of MAEE with eliminated methyl groups was produced.

### **Working Example 4**

A catalyst in which 10% by weight and 10% by weight of Ni and Cu, respectively, in terms of their metal content and 5% by weight of alumina were supported on a silica carrier was immersed for 24 hours at 60°C in PEG (average molecular weight: 1000). After thoroughly removing the excess PEG, the catalyst was packed into a Pyrex tubular reactor and heated to 190°C in a hydrogen stream under atmospheric pressure. A mixed solution comprising 1 part (by weight) of DEG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 560 hr<sup>-1</sup>. Hydrogen was supplied in a quantity 54 times the



amount of DEG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 42%, the selectivity was 74.7% for DMAEE and 13.3% for BDMAEE, and no MAEE with eliminated methyl groups was produced.

### **[0031] Comparative Example 3**

A catalyst in which 10% by weight and 10% by weight of Ni and Cu, respectively, in terms of their metal content and 5% by weight of alumina were supported on a silica carrier was pulverized without being immersed in PEG. One gram of this catalyst and 30 g of DEG were placed in a Pyrex vessel, and 100 mL/min of hydrogen and 150 mL/min of DMA (anhydrous) were supplied thereto under stirring and heated to 190°C. The liquid-phase reaction was continued long enough (6 hours) to obtain substantially the same DEG conversion rate as in working example 4 while removing the water produced under atmospheric pressure during the reaction. As a result of subsequent cooling and analysis of the product solution by gas chromatography, the DEG conversion rate was 42%, the selectivity was 87.6% for DMAEE and 9.7% for BDMAEE, and 1.0% MAEE with eliminated methyl groups was produced.

### **[0032] Working Example 5**

A catalyst in which 15% by weight, 10% by weight, and 4% by weight of Ni, Co, and Cu, respectively, in terms of their metal content and 5% by weight of alumina were supported on a silica carrier was immersed for 24 hours at 60°C in methoxypolyethylene glycol (molecular weight: 550). After removing the excess methoxypolyethylene glycol, the catalyst was packed into a Pyrex tubular reactor and heated to 220°C in a hydrogen stream under atmospheric pressure. A mixed solution comprising 1 part (by weight) of DEG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 5700 hr<sup>-1</sup>. Hydrogen was supplied in a quantity 12.7 times the amount of DEG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the DEG conversion rate was 7%, the selectivity was 79.2% for DMAEE and 5.8% for BDMAEE, and no MAEE with eliminated methyl groups was produced.

### **[0033] Working example 6**

A catalyst in which 10% by weight and 10% by weight of Ni and Cu, respectively, in terms of their metal content and 5% by weight of alumina were supported on a silica carrier was

immersed for 24 hours at 60°C in PEG (average molecular weight: 1000). After thoroughly removing the excess PEG, the catalyst was packed into a Pyrex tubular reactor and heated to 200°C in a hydrogen stream under atmospheric pressure. A mixed solution comprising 1 part (by weight) of EG, 4 parts of DMA, and 6 parts of water was gasified and supplied thereto. The gas space velocity at this time was set at 180 hr<sup>-1</sup>. Hydrogen was supplied in a quantity 24 times the amount of EG in terms of the molar ratio. As a result of analysis of the product by gas chromatography, the EG conversion rate was 78%, and the selectivity was 56.8% for DMAE and 43.2% for TMEDA. No product with eliminated methyl groups was seen.

**[Merits of the Invention]** The present invention provides an amination process that is capable of adequately suppressing elimination and transfer of the alkyl groups under low pressure, and of aminating low-boiling alcohols, and is thus of great significance.

(Continued from front page)

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